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New light on EuO thin films

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Chapter 5

Temperature-dependent exchange splitting in EuO

The temperature dependence of the x-ray absorption spectrum near the O K edge in single crystals of the ferromagnetic semiconductor EuO is studied. Clear signatures of an exchange splitting proportional to the long range magnetic order are observed in the XAS spectra. This temperature dependence is very different from that of the optical absorption edge, which was generally believed to be a measure of the exchange splitting. The present results contradict this and lead to the conclusion that the temperature dependent exchange splitting of conduction band electrons in EuO is similar to that in Gd metal despite the different origin of the magnetic interactions in these materials.

5.1 Introduction

Since their discovery [49, 50] around 1960, the properties of ferromagnetic semiconductors have continuously fascinated scientists. The magnetic order in this class of compounds is induced by indirect and superexchange interactions [53] and is thus of a different origin than the itinerant electron ferromagnetism of the elemental ferromagnets. The transition to the magnetically ordered state is accompanied by large changes in transport and magneto-optical properties, which include colossal magnetoresistance and a giant Kerr-effect. Moreover, a giant red-shift in the optical absorption edge is observed upon entering the ferromagnetic state of EuO [76]. This shift appeared to be a universal feature of ferromagnetic semiconductors [64, 67, 188, 189] and has been attributed to a splitting of the conduction band as a result of the exchange interactions between localized magnetic moments and conduction electrons. Remarkably this temperature dependent red-shift does not follow the long range order and part of the shift is even realized above the Curie temperature (see figure 1.6(a)). This part of the shift in the paramagnetic state has generally been ascribed to a splitting or lowering of the conduction band

due to interactions between conduction band electrons and spin-fluctuations in the paramagnetic state [9, 10, 12, 92–94].

More recent developments in photo-electron spectroscopy techniques have allowed direct observation of the exchange splitting, a characteristic parameter in most models for ferromagnetism. During the last decades this has resulted in intensive efforts to measure the temperature dependence of this splitting in the elemental ferromagnets. These studies have shown that the temperature dependence of the Gd $5d$ bands is well described by an exchange splitting which follows the long range magnetization [190–193]. However more locally sensitive spectroscopies show that short range order induces a local exchange splitting which can persist even above T_c [194, 195]. For the elemental transition metal ferromagnets with their narrower $3d$ bands the situation seems to be even more complicated, with an exchange splitting which persists in the paramagnetic state for some bands and collapses at T_c for others [196].

Although the ferromagnetic exchange interactions in stoichiometric EuO are not mediated by itinerant electrons like in Gd metal, but by virtual excitations of valence electrons [10, 53], similarities are still expected as in both materials the magnetic interactions which split the conduction band are mainly generated by the ferromagnetic alignment of the $4f$ spins. However the strong differences between the temperature dependence of the red-shift in EuO and that of the exchange splitting in Gd metal seem to suggest otherwise.

To clarify this issue we present temperature dependent O K x-ray absorption spectroscopy (XAS) data on single crystals of EuO. We show strong evidence that the exchange splitting of the Eu $5d$ conduction band *does* follow the long range magnetic order. In contrast to optical absorption measurements we do not find evidence for a splitting above the Curie temperature. We discuss these results and point out important differences between the interpretation of data obtained with optical and x-ray photon energies.

5.2 Experimental

Stoichiometric single crystals of EuO were grown by a solution sintering process [16]. Measurements were performed using the Dragon beamline at the Synchrotron Radiation Research Center (SRRC) in Taiwan. The crystals were cleaved *in situ* after which x-ray absorption spectra were recorded in fluorescence yield mode. The resolution of the x-rays was ~ 0.2 eV. In the upper panel of figure 5.1 we show O K XAS spectra taken above and below the Curie temperature ($T_c = 69$ K). This technique probes the O $2p$ character of the conduction band, which is present as a result of covalent mixing between the O $2p$ and Eu $5d - 6s$ orbitals. The spectra are very similar to those observed on thin EuO films in total electron yield mode (compare with figure 4.2). However in fluorescence yield on single crystals the feature at 529.5 eV related to surface defects is absent, due to the lower surface sensitivity of

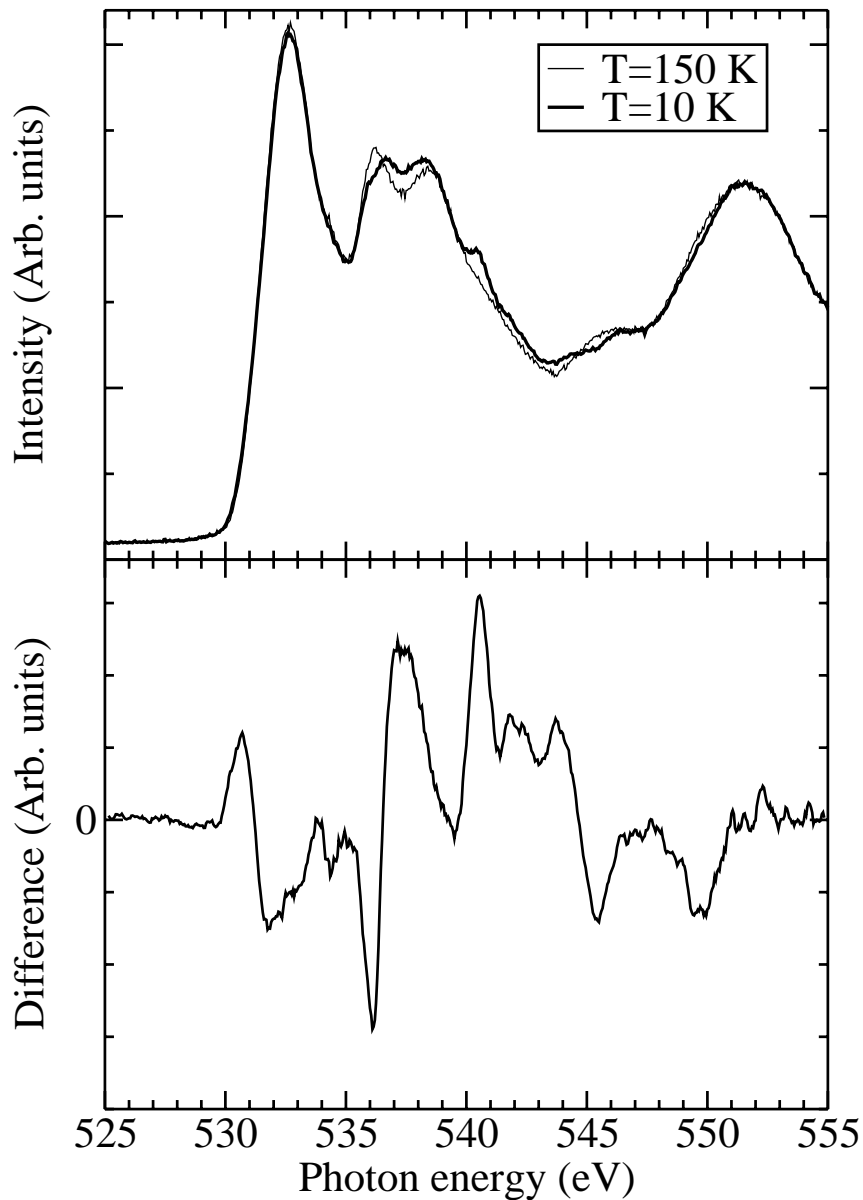


Figure 5.1: *Upper panel: O K XAS spectrum at 10 K and 150 K of a EuO single crystal. Lower panel: Difference data (smoothed) between the intensity at 10 K and 150 K.*

this technique and possibly due to a higher stoichiometry of the single crystals. Clear changes are observed upon lowering the temperature. To highlight these changes, the difference spectrum is plotted in the lower panel of figure 5.1. Interestingly the maxima in the high temperature spectrum generally seem to coincide with the minima of the difference spectrum, indicative of a splitting or broadening of spectral weight. The feature at 536.2 eV which transforms into two peaks at low temperature

strongly suggests that it concerns a splitting. The splitting may also be present in the main peak at 532.7 eV, but it is less obvious here due to the larger intrinsic width of this peak. Spin-resolved XAS measurements [175] indeed confirmed that these changes in the XAS spectrum are strongly related to a spin splitting of the spin-up and spin-down density of states due to the $4f - 5d$ exchange interaction. On the other hand the peaks which appear in the ferromagnetic state between 540.0 and 543.0 eV do not follow this behavior and are probably related to changes in the unoccupied Eu $4f$ density of states. Qualitative agreement was found between the x-ray absorption spectrum and the density of states as obtained by LSDA+U calculations (see figure 4.5). These calculations also showed that the exchange splitting depends on momentum and energy. To extract quantitative data on this splitting the bottom of the band is therefore preferable, as its density of states is not a sum of contributions from different energies or parts of the Brillouin zone.

5.3 Discussion

In the simplest mean field picture the exchange splitting can be described as follows. If $D(E)$ is the unoccupied density of states of the $5d$ conduction band in the absence of $4f - 5d$ exchange interactions, the exchange interaction Δ_{ex} will lower the spin-up levels by an energy Δ_{ex} , while the spin-down states will be raised by the same amount. The total unoccupied density of states $D'(E, \Delta_{\text{ex}})$ will thus become:

$$D'(E, \Delta_{\text{ex}}) = \frac{1}{2}(D(E + \Delta_{\text{ex}}) + D(E - \Delta_{\text{ex}})) \quad (5.1)$$

Therefore, in a one electron picture one expects the absorption spectrum to have a shape similar to $D'(E)$ if the electron is excited to the conduction band from a sharp energy level. As the valence band becomes spin-polarized in ferromagnetic state, optical spin-flip transitions are much less probable than spin-conserving transitions and the transition probabilities to the spin-up and spin-down bands are changing when the sample is magnetized*. Also, excitonic effects can play an important role, as the excited electron can increase the exchange coupling between Eu atoms in the vicinity of the $4f$ hole. This might lead to an increased local magnetization and exchange splitting inside the exciton and thus modify the position of the absorption edge. These considerations show that although the shift of the absorption edge strongly suggests the presence of exchange splitting it is not a very reliable measure of the size or temperature dependence of this splitting.

The interpretation of the O K x-ray absorption spectrum is easier because it involves excitations from a dispersionless and spinless core-level. Therefore we expect that the XAS data should approximately follow equation (5.1). To obtain a quantitative estimate of the exchange splitting from the XAS data it is thus not sufficient

*The reduction in the optical absorption peak energy in the ferromagnetic state (see figure 2.1), which is not expected from equation (5.1), might be related to this effect.

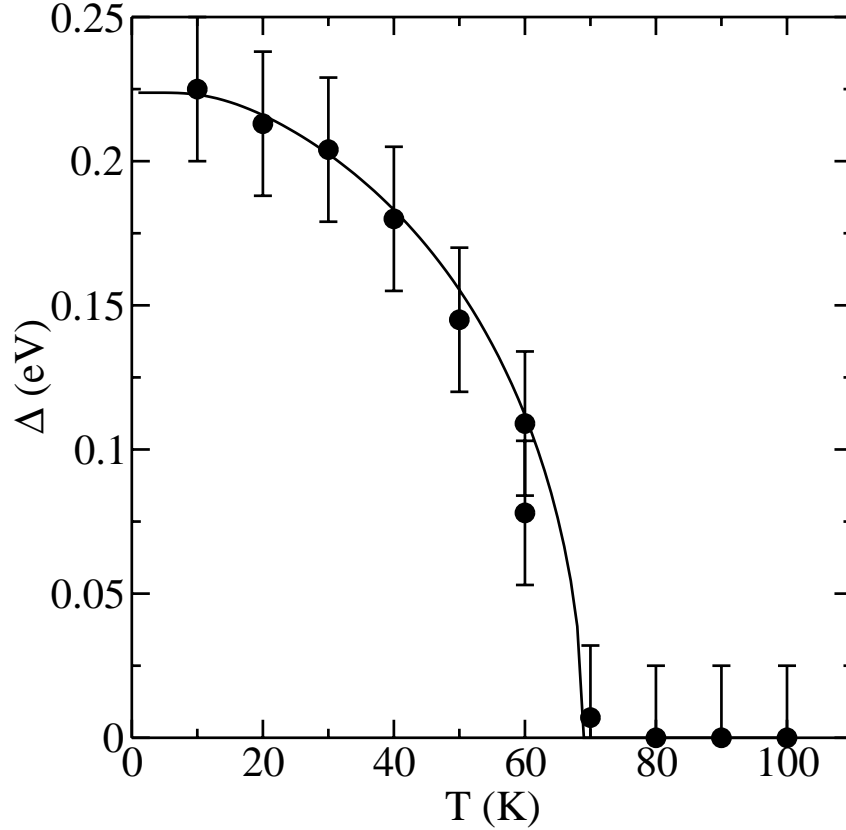


Figure 5.2: Δ_{ex} as obtained from least square fits of the low temperature data with the splitted 150 K XAS spectrum following equation (5.1). Also shown is a solid curve which has the shape of the magnetization in a mean field model for a $J = 7/2$ ferromagnet with $T_c = 69$ K.

to measure the edge shift as the measured shift will depend on the shape $D(E)$. A least squares fit of the various low temperature spectra was made in the photon energy region 529.0-534.7 eV using $D'(E, \Delta_{\text{ex}})$ according to equation (5.1), with Δ_{ex} as the only fitting parameter and $D(E)$ assumed equal to the XAS spectrum* at 150 K. Excellent fits were obtained in this energy region. To verify if a temperature independent center of gravity indeed resulted in the best fit we also fitted the spectra (in the same energy region) allowing an arbitrary energy shift in addition to the arbitrary splitting Δ_{ex} . For all spectra, best fits were obtained for shifts ≤ 0.02 eV, very near to the shift of the center of gravity as expected. In figure 5.2 we show the fitted Δ_{ex} versus temperature. A maximum splitting of $2\Delta_{\text{ex}} = 0.45$ eV is found,

*A smoothed curve of the 150 K spectrum, which was obtained by fitting it with multiple Gaussians, was used for $D(E)$ to eliminate smoothing effects when applying equation (5.1) to a discrete data set which contains statistical noise.

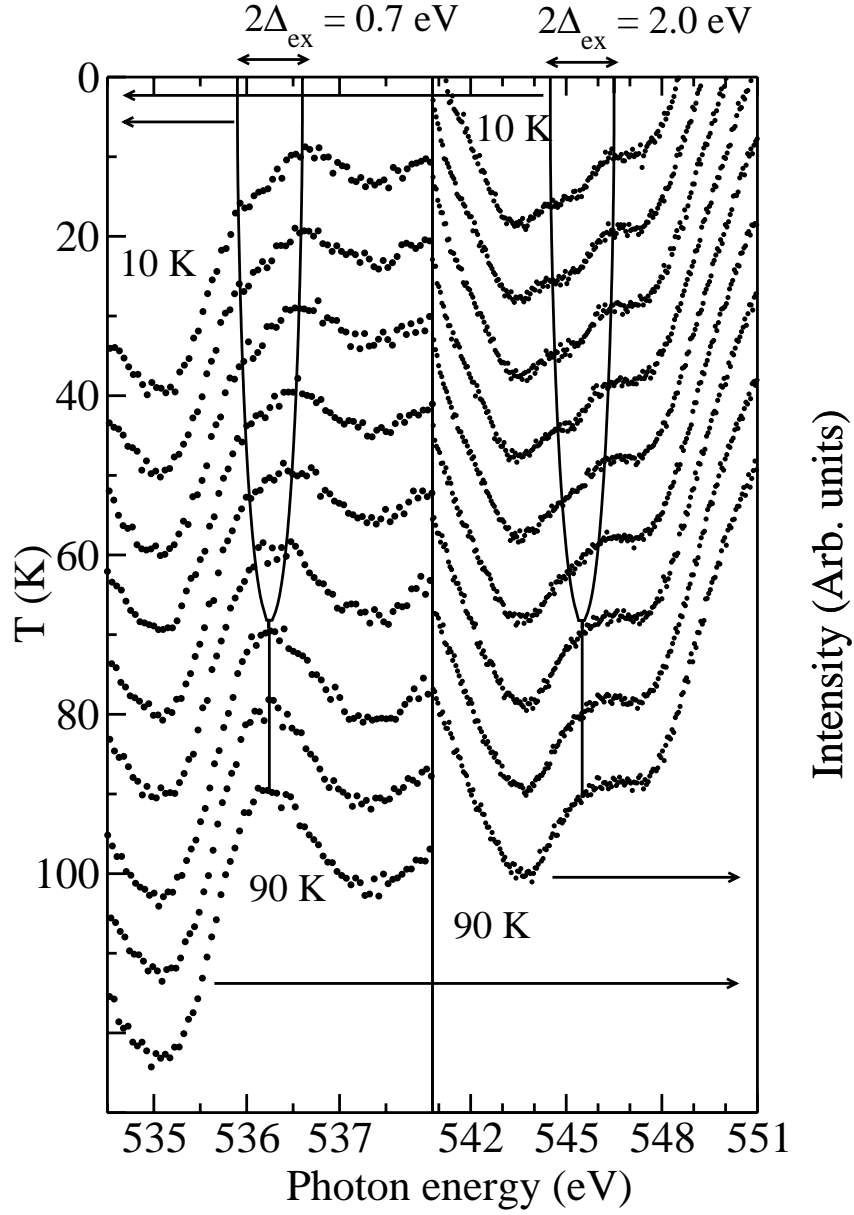


Figure 5.3: Two energy regions of the O K XAS spectra of EuO at temperatures from 10 to 90 K, taken at intervals of 10 K. Spectra are offset to align the split peak with its temperature on the left axis. Solid lines are split proportional to the magnetization in a mean field model as in figure 5.2.

which is somewhat smaller than the exchange splitting of $2\Delta_{\text{ex}} = 0.6$ eV found in the spin-polarized XAS measurements [175]. This smaller value might be due to statistical errors as a result of the fact that it is very difficult to resolve a splitting of two peaks which is smaller than their linewidth. However, the smaller value of the

Δ_{ex} might also very well be a result of differences between the mean field assumption of $S = 0$ above T_c and the actual random spin-orientation of local $S = 7/2$ moments in the paramagnetic state, which can broaden the high-temperature peak with respect to the spin-polarized peak width in the ferromagnetic state (compare figures 5.1 and 4.5). In the same figure a solid curve is plotted with the shape of the spontaneous magnetization of a $J = 7/2$ ferromagnet with $T_c = 69$ K as was obtained from solving the mean/molecular field model. The magnetization in EuO is known to follow such a mean field model to a very high accuracy (see figure 1.2 [31]). The exchange splitting as determined from the XAS data very nearly follows the calculated magnetization curve. Additional information on the exchange splitting in EuO was found by examining the temperature dependence of the split features at 536.2 eV and 545.5 eV, which are shown in figure 5.3. In the same figure solid lines split proportional to the mean field magnetization of a $J = 7/2$ ferromagnet are shown. There is clear qualitative agreement between the observed peak position and that expected from a mean field model with an exchange splitting proportional to the long range order. A maximum splitting of $2\Delta_{\text{ex}} = 0.7 \pm 0.1$ eV is observed in the peak at 536.2 eV, corresponding well to an energy separation of the spin-polarized peaks of about 0.8 eV. The peak at 545.5 eV seems to show a maximum splitting of 2.0 ± 0.1 eV, which is remarkable as it is considerably larger than the splitting predicted by LSDA+U calculations. As we have not studied this structure with spin-polarized XAS it is unclear if these large changes are due to the separation of two spin-polarized bands, or if they are related to more intricate changes in the spectral weight as a result of the ferromagnetic ordering. The XAS data above suggest that the exchange splitting in the EuO conduction band follows the long range magnetic order, with a collapse into a single band at T_c . This is in remarkable contrast to the behavior of the optical absorption edge, which does not follow the long range magnetic order [64, 67], and already starts shifting in the paramagnetic state. This shift has been subject of many theoretical studies [9, 10, 12, 92–94]. Most effort focused on calculations of the changes in the quasiparticle energy due to dressing of conduction electrons by spin-fluctuations in the paramagnetic state of the ferromagnet. The shift of the optical absorption edge in the paramagnetic state could however have a different origin as the Coulomb attraction of the $4f$ hole might localize the excited electron in an s -like orbital with radius R . Kasuya [7] suggested that the bottom of the absorption edge is formed by such a magnetic exciton. This suggestion was supported by the exponential shape of the absorption edge [67]. The radius R of this exciton might very well be of the order of the lattice constant. In this case the exchange splitting of the electron will not depend on the long range order, but on the short range order within its radius. In fact it was shown that the shift of the absorption edge follows the nearest neighbor spin-correlation function $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle / S^2$, for i and j at nearest neighbor sites, quite closely [64, 67], thus suggesting that the excited electron is more sensitive to the short-range order than to the long-range order. Indications for a similar magnetic short-range (~ 20 Å)

order above T_c were found in Gd metal [194, 195].

Unlike the local optically excited $4f - 5d$ exciton, excitonic effects are expected to be much smaller in O K XAS with the final state hole on an oxygen atom. Although on-site excitations from a core-hole can lead to large excitonic effects, the conduction band of EuO consists mainly of Eu $5d$ orbitals and the excited electron will therefore be effectively separated from the oxygen atom and thus have a much smaller Coulomb attraction to the core hole. The absence of a sharp exciton white line in the XAS spectra supports this conclusion.

5.4 Conclusions

In summary, we have investigated the conduction band of EuO by XAS. We did not find evidence for an onset of the splitting above T_c due to spin-fluctuations [9, 10, 12, 92–94]. This led us to suggest that the red-shift in the optical absorption is related to excitonic effects, as a result of which the absorption edge will follow the local order instead of the splitting experienced by conduction band electrons. In contrast to the temperature dependence of the absorption edge we found strong evidence that the temperature dependent exchange splitting in EuO follows the long-range order, similar to the exchange splitting in Gd metal.